Inorganic Chemistry

Comparison of the Coordination of $B_{12}F_{12}^{2-}$, $B_{12}CI_{12}^{2-}$, and $B_{12}H_{12}^{2-}$ to Na⁺ in the Solid State: Crystal Structures and Thermal Behavior of Na₂(B₁₂F₁₂), Na₂(H₂O)₄(B₁₂F₁₂), Na₂(B₁₂CI₁₂), and Na₂(H₂O)₆(B₁₂CI₁₂)

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Supporting Information

ABSTRACT: The synthesis of high-purity Na₂B₁₂F₁₂ and the crystal structures of Na₂(B₁₂F₁₂) (5 K neutron powder diffraction (NPD)), Na₂(H₂O)₄(B₁₂F₁₂) (120 K single-crystal X-ray diffraction (SC-XRD)), Na₂(B₁₂Cl₁₂) (5 and 295 K NPD), and Na₂(H₂O)₆(B₁₂Cl₁₂) (100 K SC-XRD) are reported. The compound Na₂(H₂O)₄(B₁₂F₁₂) contains {[(Na(μ -H₂O)₂Na(μ -H₂O)₂)]²⁺}_∞ infinite chains; the compound Na₂(H₂O)₆(B₁₂Cl₁₂) contains {[(Na(μ -H₂O)₂Na(μ -H₂O)₂Na(μ -H₂O)₂Na(μ -O)₆)]²⁺ cations with OH···O hydrogen bonds linking the terminal H₂O ligands. The structures of the two hydrates and the previously published structure of Na₂(H₂O)₄(B₁₂H₁₂) are analyzed with respect to the relative coordinating ability of B₁₂F₁₂²⁻, B₁₂H₁₂²⁻, and B₁₂Cl₁₂²⁻ toward Na⁺ ions in the solid state (i.e., the relative ability of these anions to satisfy the valence of Na⁺). All three hydrated structures have



distorted octahedral NaX₂(H₂O)₄ coordination spheres (X = F, H, Cl). The sums of the four Na–O bond valence contributions are 71, 75, and 89% of the total bond valences for the X = F, H, and Cl hydrated compounds, respectively, demonstrating that the relative coordinating ability by this criterion is $B_{12}Cl_{12}^{2-} \ll B_{12}H_{12}^{2-} < B_{12}F_{12}^{2-}$. Differential scanning calorimetry experiments demonstrate that Na₂(B₁₂F₁₂) undergoes a reversible, presumably order–disorder, phase transition at ca. 560 K (287 °C), between the 529 and 730 K transition temperatures previously reported for Na₂(B₁₂H₁₂) and Na₂(B₁₂Cl₁₂), respectively. Thermogravimetric analysis demonstrates that Na₂(H₂O)₄(B₁₂F₁₂) and Na₂(H₂O)₆(B₁₂Cl₁₂) undergo partial dehydration at 25 °C to Na₂(H₂O)₂(B₁₂F₁₂) and Na₂(H₂O)₂(B₁₂Cl₁₂) in ca. 30 min and 2 h, respectively, and essentially complete dehydration to Na₂(B₁₂F₁₂) and Na₂(B₁₂Cl₁₂) within minutes at 150 and 75 °C, respectively (the remaining trace amounts of H₂O, if any, were not quantified). The changes in structure upon dehydration and the different vapor pressures of H₂O needed to fully hydrate the respective Na₂(B₁₂X₁₂) compounds provide additional evidence that $B_{12}Cl_{12}^{2^-}$ is more weakly coordinating than $B_{12}F_{12}^{2^-}$ to Na⁺ in the solid state. Taken together, the results suggest that the anhydrous, halogenated *closo*-borane compounds Na₂(B₁₂F₁₂) and Na₂(B₁₂Cl₁₂), in appropriately modified forms, may be viable component materials for fast-ion-conducting solid electrolytes in future energy-storage devices.

INTRODUCTION

Salts of polyhedral borane and carborane anions and metal ions from across the periodic table have numerous applications, ranging from electrolytes to catalysts to hydrogen or ammonia storage, to carriers for the delivery of boron clusters into cancer cells.^{1–9} This includes the halogenated derivatives of these anions, which have been shown to be chemically and electrochemically robust as well as weakly coordinating.^{10–16}

We have studied the structures and physicochemical properties of anhydrous, hydrated, and solvated salts of $B_{12}F_{12}^{2-}$, a highly symmetric, very-weakly coordinating (i.e., superweak¹⁷) anion, including $K_2(B_{12}F_{12})$,¹⁸

 $K_2(H_2O)_4(B_{12}F_{12}),^{14}$ $K_2(HF)_3(B_{12}F_{12}),^{19}$ $K_2(solv)_n(B_{12}F_{12})$ (solv = H_2O_2 , CH_3CN , CH_3OH , $CH_3NO_2),^{20}$ and $M_2(SO_2)_6(B_{12}F_{12})$ (M = Ag, K).^{21} These compounds can serve as models for metal-ion solvation in liquid-anhydrous $HF,^{22}$ $H_2O,^{23-25}$ $SO_2,^{26}$ etc. or for metal-ion solvation in metal–organic frameworks (MOFs),^{27-30} zeolites,^{31-35} biological metal-ion channels,^{36} and concentrated aqueous salt solutions.^{37} The hydrated and anhydrous structures can serve as reference points for reversible hydration/dehydration thermo-

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Table 1. Crystal Data and Final Refinement	Parameters for Single-Crystal X-ray	y and Neutron Powder Diffraction Structures
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compound abbreviation	$Na_2(B_{12}F_{12})$	$Na_2(H_2O)_4(B_{12}F_{12})$	$Na_2(B_{12}Cl_{12})$	$Na_2(B_{12}Cl_{12})$	$Na_2(H_2O)_6(B_{12}Cl_{12})$
formula	$B_{12}F_{12}Na_2$	$B_{12}F_{12}H_8Na_2O_4$	$B_{12}Cl_{12}Na_2$	$B_{12}Cl_{12}Na_2$	$B_{12}Cl_{12}H_{12}Na_2O_6$
formula wt, g mol ⁻¹	403.68	475.76	601.14	601.14	709.20
SC-XRD or NPD	NPD	SC-XRD	NPD	NPD	SC-XRD
diffraction wavelength, Å	1.5397	0.710 73	1.5398	1.5397	0.710 73
<i>Т,</i> К	5(2)	120(2)	5(2)	295(2)	100(2)
crystal system	hexagonal	triclinic	cubic	cubic	monoclinic
space group, Z	P3, 3	<i>P</i> 1, 4	<i>Pa</i> 3, 4	<i>Pa</i> 3, 4	C2/c, 4
<i>a,</i> Å	12.0118(13)	10.6491(10)	12.4694(4)	12.5577(9)	16.1546(14)
b, Å	12.0118(13)	10.8501(10)	12.4694(4)	12.5577(9)	8.9220(8)
<i>c,</i> Å	7.3347(15)	13.8432(11)	12.4694(4)	12.5577(9)	17.9687(16)
α , deg	90	96.813(3)	90	90	90
β , deg	90	96.479(3)	90	90	94.999(4)
γ, deg	120	91.347(4)	90	90	90
<i>V</i> , Å ³	916.5(1)	1577.0(2)	1938.8(2)	1980.3(4)	2580.0(4)
$ ho_{ m calc}$ g cm ⁻³	2.194	2.004	2.059	2.016	1.826
$R(F) \ (I > 2\sigma(I))^b$	0.0317	0.0666	0.0191	0.0156	0.0225
$wR(F^2)$ [all data] ^b	0.0388	0.2163	0.0236	0.0186	0.0515
GOF	1.10	1.046	1.04	0.93	1.071
All results from this work unle	ess otherwise indicate	d. ${}^{b}R(F) = \sum F_0 - F_c /$	$\sum F_0 $: $wR(F^2) = (\sum$	$\sum \left[w (F_0^2 - F_c^2)^2 \right] / \sum$	$[w(F_0^2)^2])^{1/2}$.

dynamic and kinetic studies that are important with respect to the use of salt hydrates for the storage of low-potential heat from solar energy. $^{38-41}$

We have also studied anhydrous Li⁺ and Na⁺ salts of $B_{12}H_{12}^{2-}$ and related polyhedral borane and carborane anions. Many of these compounds exhibit alkali-metal superionic conductivity above their respective order-disorder phasetransition temperatures, which are, for example, 256 °C for $Na_{2}(B_{12}H_{12})$,⁴² 110 °C for $Na_{2}(B_{10}H_{10})$,⁴³ 107 °C for $Na(CB_{11}H_{12})$,⁴⁴ and room temperature, 24 °C, for Na-(CB₉H₁₀).⁴⁵ These materials hold promise as solid-state electrolytes for secondary alkali-metal-ion batteries. The favorable superionic disordered structures formed for the closo-hydroborane and closo-hydrocarborane salts with small Li⁺ and Na⁺ cations are the result of the particularly significant differences in the sizes of the cations and anions. In the absence of solvating molecules such as H₂O, there is a proclivity for the small cations to favor lower coordination with the surrounding overly large anions to approach them more closely, thereby maximizing the stabilizing Coulombic interactions.⁴⁶ In general, the order/disorder phase transitions exhibited by the anhydrous hydroborane and hydrocarborane salts of Li⁺ and Na⁺ are firstorder, and the highly orientationally disordered and highly orientationally mobile anions in the disordered phases typically form cubic (face-centered cubic (FCC) or body-centered cubic (BCC)) or hexagonal packing arrangements.^{42–46} The resulting interstitial network allows for extremely facile diffusion of a liquid-like cation sublattice and thus dramatically high ionic conductivities.

Hence, it is reasonable to assume that anhydrous alkali-metal salts of the even larger weakly coordinating halogenated borane and carborane anions might also exhibit superionic conductivity in entropically driven higher-temperature disordered phases, especially for their salts with the smallest alkali-metal cations Li^+ and Na^+ . Moreover, it is possible that their hydrated salts will undergo reversible dehydration at practical rates and at practical temperatures. In preparation for such studies, we investigated the structures and thermal behavior of anhydrous and hydrated $\mathrm{Na}_2(\mathrm{B}_{12}\mathrm{F}_{12})$ and $\mathrm{Na}_2(\mathrm{B}_{12}\mathrm{Cl}_{12})$. The results are reported herein. The structures are compared and contrasted

with the previously reported structures of $Na_2(B_{12}D_{12})^{47}$ and $Na_2(H_2O)_4(B_{12}H_{12})$.⁴⁸ Among other things, the new structures have allowed the weakly coordinating nature of $B_{12}H_{12}^{2-}$, $B_{12}F_{12}^{2-}$, and $B_{12}Cl_{12}^{2-}$ in the solid state to be directly compared quantitatively for the first time.

EXPERIMENTAL METHODS

Reagents and General Procedures. Anhydrous compounds were prepared using standard airless-ware glassware and a Schlenkstyle vacuum line and were stored in a nitrogen-filled glovebox.⁴ Potassium dodecafluoro-closo-dodecaborate(2-), $K_2(B_{12}F_{12})$, was synthesized by the direct fluorination of $K_2(B_{12}H_{12})$ with 80:20 N_2/F_2 in CH₃CN at 0 °C and purified as previously described.^{20,50,51} [*Caution*! The original purification procedure^{50,51} involving H_2O_2 in the purification stage is not recommended because of the potential isolation of explosive $K_2(H_2O_2)_x(H_2O)_{2-x}(B_{12}F_{12})^{20}$ An alternate, safer procedure² is recommended.] The substitution of F atoms for H atoms was monitored periodically using negative-ion electrospray-ionization mass spectrometry (NI-ESI-MS). The final degree of F/H metathesis, determined by NI-ESI-MS as well as by ¹⁹F{¹¹B} and ¹¹B{¹⁹F} NMR spectroscopy, was found to be 99.5+%. Recrystallization from water removed a trace amount of BF₄⁻ that was present. It is important to remove BF₄⁻ contamination from the potassium salt, because it is more difficult to remove BF_4^- from $Na_2(B_{12}F_{12})$ by recrystallization. Distilled water was deionized with a Barnstead Nanopure system. [The mention of all commercial suppliers in this paper is for clarity. This does not imply the recommendation or endorsement of these suppliers by NIST.] The deionized distilled water (dd-H₂O) had a resistivity greater than or equal to 18 M Ω (all samples of H₂O used in this work correspond to dd-H₂O prepared in this way). Sodium chloride (NaCl; Macron, ACS Reagent grade; lot J52619) and Na₂(B₁₂Cl₁₂) (Katchem, Prague, Czech Republic) were used as received.

Anhydrous $Na_2(B_{12}Cl_{12})$ and Crystallization of $Na_2(H_2O)_6(B_{12}Cl_{12})$. Residual coordinated water was removed from $Na_2(B_{12}Cl_{12})$ by heating under vacuum at 160 °C for 16 h. The remaining trace amount of H_2O , if any, was not quantified (see below). Recrystallization from dd- H_2O (slow evaporation during two weeks) afforded crystals of $Na_2(H_2O)_6(B_{12}Cl_{12})$ suitable for single-crystal X-ray diffraction (SC-XRD).

High-Purity Anhydrous $Na_2(B_{12}F_{12})$ and $Na_2(H_2O)_4(B_{12}F_{12})$. An aqueous solution of $K_2(B_{12}F_{12})$ was converted to $Na_2(B_{12}F_{12})$ using Purolite UCW 9126 cation-exchange resin. The ion-exchange column was prepared using a 10 wt % solution of ACS Reagent grade NaCl

compound	$Na_2(B_{12}F_{12})$	$Na_2(H_2O)_4(B_{12}F_{12})$	$Na_2(B_{12}Cl_{12})$	$Na_2(H_2O)_6(B_{12}Cl_{12})$	$Na_2(B_{12}D_{12})^b$	$Na_2(H_2O)_4(B_{12}H_{12})^c$
Na-X(B)	$2.29(3) - 2.44(3)^d$	$2.313(8) - 2.381(7)^d$	2.86(1), 2.896(6) ^e	$3.0928(4) - 3.3108(4)^{e}$	$2.25(1) - 2.88(1)^{f}$	2.405-2.936 ^f
Na-O		2.368(9)-2.473(9)		2.220(1)-2.393(1)		2.368-2.413
$\sum_{valences}^{Na-X bond}$	0.92 ^d	$0.28 - 0.34^d$	0.84^{e}	0.15 (Na1), 0.09 Na(2) ^e	1.05 ^f	0.26–0.28 ^f
$\sum_{valences}^{(Na-O bond}$		0.73-0.79		0.91 (Na1), 1.09 (Na2)		0.81-0.83
Σ(Na bond valences)	0.92	1.01-1.14	0.84	1.06 (Na1), 1.18 (Na2)	1.05	1.07-1.10
Na…⊙	4.37-5.36	5.04-6.30	5.15×3	$5.78 \times 2 \text{ (Na1)};^{\text{g}} 6.43 \times 2,$ $6.59 \times 2 \text{ (Na2)}$	4.05-5.45	3.49, 3.65
$\odot \cdots \odot^h$	7.32-8.55	6.89-8.80	8.82×12	8.99 × 2, 10.03 × 4	6.98-7.39	6.72-7.88
ave $\odot \cdots \odot^h$	7.79	7.82	8.82	9.69	7.13	7.44
$\odot \cdots \odot \cdots \odot^h$	54.2-71.4	49.2-73.7	60	52.8 × 3, 63.6 × 3	57.8-63.6	50.8-68.1
$\perp \odot_6 \cdots \odot_6^i$	6.01	7.69	7.20	8.05	5.78	7.04
closest Na…Na	5.28, 5.37	3.558(6)-3.609(6)	5.66	3.544(1)	4.33, 4.85	3.491, 3.650
B-X	$1.38(2) - 1.40(2)^d$	$1.34(1) - 1.37(1)^d$	$1.791(1) - 1.796(1)^{e}$	$1.786(1) - 1.800(1)^{e}$	$1.208(3) \times 12^{f}$	$1.01 - 1.12^{f}$
В-В	1.73(1) - 1.83(1)	1.77(2) - 1.82(2)	1.771(2) - 1.794(1)	1.784(2) - 1.793(1)	$1.776(2) \times 30$	1.769-1.790

^{*a*}All results from this work unless otherwise noted. The results listed for $Na_2(B_{12}Cl_{12})$ are from the 5 K NPD structure determination. ^{*b*}Reference 47. ^{*c*}Reference 48. Uncertainties in interatomic distances were not reported in this dissertation, and no CIF has been deposited. ^{*d*}X = F. ^{*c*}X = Cl. ^{*f*}X = D or H. ^{*g*}The next two closest Na1…O distances are 7.514 Å. ^{*h*}These distances or angles are within the hexagonal planes of B₁₂ centroids (Os). ^{*i*}Perpendicular distance between close-packed planes of B₁₂ centroids.

(the maximum allowable amounts of $K^{\scriptscriptstyle +},\,Mg^{2\scriptscriptstyle +},\,and~Ca^{2\scriptscriptstyle +}$ listed were 0.007, 0.003, and 0.003 mol %, respectively). After a single pass through the ion-exchange column, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis demonstrated that the sodium salt contained 0.021 mol % K⁺, 0.040 mol % Li⁺, 0.0010 mol % Mg²⁺, and 0.000 24 mol % Ca²⁺. All other metal ions present had concentrations less than 0.01 mol %. A second treatment with a freshly prepared sodium-regenerated column reduced the amount of K⁺ to less than 0.007 mol %. Anhydrous $Na_2(B_{12}F_{12})$ was isolated from the purified aqueous solution by rotary evaporation followed by heating at 175-180 °C under vacuum for 24 h. A sample of Na₂(B₁₂F₁₂) dried in this way completely dissolved in CD₃CN, and ${}^{11}B{}^{19}F{}$ and ${}^{19}F{}^{11}B{}$ NMR spectra demonstrated that a negligible amount of H₂O was present and that the $B_{12}F_{12}^{2-}$ anion was intact (i.e., no degradation had occurred; see Supporting Information). The remaining trace amount of H₂O, if any, could not be quantified, because a ¹H NMR spectrum in CD₃CN showed a small peak due to H₂O that could not be distinguished from contamination by the ca. 1 ppm of water vapor present in the glovebox nitrogen atmosphere. The yield of high-purity anhydrous $Na_2(B_{12}F_{12})$ was greater than 95% based on $K_2(B_{12}F_{12})$. Recrystallization from water afforded crystals of $Na_2(H_2O)_4(B_{12}F_{12})$ suitable for single-crystal diffraction. It is possible that the use of a higher-purity grade of NaCl would result in even less contamination with Li⁺, K⁺, and other metal ions.

Inductively Coupled Plasma Atomic Emission Spectroscopy. Metal analyses were performed using a PerkinElmer Model 7300 DV ICP-OES, ICP-AES instrument. Elements analyzed for each sample were Ag, Al, As, Au, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, S, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, U, V, W, Zn, and Zr. Samples were diluted in a mixture of metal-free acids (1% v/v hydrochloric acid and 5% v/v nitric acid) to a known concentration, and the reported values were an average of three replicate measurements. Ytterbium was used as an internal standard, and 15 interelement standards were used to correct for easily ionizable elements.

Differential Scanning Calorimetry (DSC). DSC measurements were performed on 3-5 mg samples of $Na_2(B_{12}F_{12})$ in aluminum sample pans under a dry He purge using Netzsch STA 449 F1 Jupiter DSC-TGA instrumentation. The heating/cooling rate was 20 K min⁻¹.

Thermogravimetric Analysis (TGA). Samples for TGA (Pt samples pans, 14–16 mg powdered samples) were analyzed using TA Instruments TGA Q500 instrumentation. Dry N₂ was used as the purge gas at a flow rate of 60 mL min⁻¹. Samples were held isothermally or heated at a rate of 10 °C min⁻¹.

Single-Crystal X-ray Diffraction (SC-XRD). Data sets for Na₂(H₂O)₄(B₁₂F₁₂) and Na₂(H₂O)₆(B₁₂Cl₁₂) were collected in Fort Collins at 120(2) and 100(2) K, respectively, using a Bruker Kappa APEX II CCD diffractometer employing Mo K α radiation and a graphite monochromator. Table 1 lists relevant data collection parameters and refinement results. Table 2 lists selected interatomic distances and bond valence (bv) values, including distances and angles involving the B₁₂ centroids (hereinafter denoted with the symbol \odot). Other information about data collection, absorption, and other corrections, structure refinement, H atom positions, etc. are included in the Supporting Information. For comparison, Table 2 also includes results for the previously reported SC-XRD structure of Na₂(H₂O)₄(B₁₂H₁₂).⁴⁸

X-ray Powder Diffraction (XRPD). Preliminary XRPD patterns for phase identification and indexing were collected for $Na_2(B_{12}F_{12})$ and $Na_2(B_{12}Cl_{12})$ in quartz capillaries using a Rigaku Ultima III X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å).

Neutron Powder Diffraction (NPD). Data sets for $Na_2(B_{12}F_{12})$ and Na₂(B₁₂Cl₁₂) were collected at the NIST Center for Neutron Research at 5 or 295 K using a BT-1 High-Resolution Powder Diffractometer at an incident neutron wavelength of 1.5398(2) Å with a Cu(311) monochromator. Because of the presence of highly neutron-absorbing ¹⁰B in the naturally occurring boron samples, diffraction patterns were measured in vanadium cans using thin annular sample geometries. For each compound, the outer annular diameter was 12 mm, and the sample thickness within the annular double-wall cavity was ca. 1 mm. Rietveld model refinements⁵² were performed using the GSAS package.53 Table 1 lists relevant data collection parameters and refinement results. Table 2 lists selected interatomic distances and bond valence (bv) values. Other information about the NPD data collections and structure refinements are included in the Supporting Information. For comparison, Table 2 also includes results for the previously reported 7 K NPD structure of $Na_2(B_{12}D_{12})$.⁴⁷ The 5K NPD patterns for $Na_2(B_{12}F_{12})$ and $Na_2(B_{12}Cl_{12})$ are shown in Figure 1. The 295 K NPD pattern for $Na_2(B_{12}Cl_{12})$ is shown in Figure S1.

Density Functional Theory Calculations. To assist the structural refinements, first-principles DFT calculations within the plane-wave implementation of the generalized gradient approximation were performed using a Vanderbilt-type ultrasoft potential with Perdew–Burke–Ernzerhof exchange correlation.⁵⁴ A cutoff energy of 544 eV and a 2 \times 2 \times 2 k-point mesh (generated using the Monkhorst–Pack scheme) were used and found to be sufficient for the total energy to converge within 0.01 meV/atom.



Figure 1. Experimental (O), fitted (red trace), and difference (black trace) NPD patterns for $Na_2(B_{12}F_{12})$ (top) and $Na_2(B_{12}Cl_{12})$ (bottom) at 5 K. Vertical bars are the calculated positions of NPD Bragg peaks for $Na_2(B_{12}F_{12})$ or $Na_2(B_{12}Cl_{12})$ (upper set of bars) and for the vanadium sample holder (lower set of bars). Standard uncertainties are commensurate with the observed scatter in the data. See Table 1 for additional information.

RESULTS AND DISCUSSION

Neutron Powder Diffraction (NPD) and Single-Crystal X-ray Diffraction (SC-XRD) Structures. Preliminary roomtemperature powder X-ray diffraction patterns for $Na_2(B_{12}F_{12})$ and $Na_2(B_{12}Cl_{12})$ were indexed to space groups $P\overline{3}$ and $Pa\overline{3}$, respectively. Both structures were then solved using direct methods. DFT calculations were performed to optimize the $B_{12}F_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$ rigid-body configurations and Na⁺ ion positions. The DFT-relaxed structural models were confirmed by Rietveld refinement using the 5 K NPD patterns, which are shown in Figure 1. For each compound, the neutron scattering Fourier difference map indicated no other possible Na⁺ site except for the DFT-predicted lowest-energy position. Minor diffraction peaks were observed from the weakly Braggscattering vanadium sample holders. The anion rigid-bond restrictions were removed during final refinement of the NPD data. The thermal parameters of like atoms were constrained to be the same. The B, F, Cl, and Na coordinates, with restraints on B-F, B-Cl, and B-B distances, and the lattice parameters were refined. See Table 1 and Supporting Information for information about the 295 K $Pa\overline{3}$ NPD structure of $Na_2(B_{12}Cl_{12})$, which will not be discussed further in this paper.

The structures of $Na_2(B_{12}F_{12})$, $Na_2(B_{12}Cl_{12})$, $Na_2(H_2O)_4(B_{12}F_{12})$, and $Na_2(H_2O)_6(B_{12}Cl_{12})$ are shown in Figures 2–4, which also include the previously reported structures of $Na_2(B_{12}D_{12})^{47}$ and $Na_2(H_2O)_4(B_{12}H_{12})^{48}$ for comparison. (There are two other previous reports of the structure of $Na_2(H_2O)_4(B_{12}H_{12})$, but in both cases there is significant disorder of the Na^+ ions and H_2O ligands.^{55,56})



Figure 2. Drawings showing the hexagonal arrays of B₁₂ centroids (large spheres) and the Na⁺ ions (small shaded spheres) in the structures of Na₂(B₁₂D₁₂), Na₂(B₁₂F₁₂), and Na₂(B₁₂Cl₁₂). Both the upper and lower sets of three drawings are to scale. The proximate Na⁺ ions that share the octahedral interstices in Na₂(B₁₂Cl₁₂) are joined with solid (upper drawing) or dashed lines (lower drawing) as visual aids, which have no other significance. These Na⁺ ions are 5.66 Å apart.

Previously reported DFT calculations have predicted that the B–B bonds in I_h -B₁₂F₁₂²⁻, at 1.794 Å (PBE0/def2-TZVP(-f)),⁵⁰ are longer than the 1.786 B–B bonds in I_h -B₁₂Cl₁₂²⁻ (PBE0/def2-TZVPP).⁵⁷ The B–B distances in the structure of Na₂(H₂O)₆(B₁₂Cl₁₂) are more precise than in previous structures containing the B₁₂Cl₁₂²⁻ anion,^{12,58} allowing a direct comparison to be made with the most precise structure reported for the B₁₂F₁₂²⁻ anion, which is K₂(H₂O)₄(B₁₂F₁₂).⁴

A plot of the experimental B–B distances at the $\pm 3\sigma$ level of confidence and the DFT-predicted B–B distance for each ion is shown in Figure 5, which also includes thermal-ellipsoid drawings of the B₁₂F₁₂^{2–} anion in K₂(H₂O)₄(B₁₂F₁₂) and the B₁₂Cl₁₂^{2–} anion in Na₂(H₂O)₆(B₁₂Cl₁₂). This plot is the first statistically significant experimental demonstration that the B₁₂ core in B₁₂F₁₂^{2–} is indeed marginally larger than the B₁₂ core in B₁₂Cl₁₂^{2–}.

The $P\overline{3}$ structure of $Na_2(B_{12}F_{12})$ consists of two unique $B_{12}F_{12}^{2-}$ anions. The one that is generated from B1, B2, F1, and F2 sits on a crystallographic $\overline{3}$ position, and the one that is generated from B3-B6 and F3-F6 sits on a crystallographic 3 position. There are twice as many B3-B6 anions as B1/B2 anions. There is only one unique Na⁺ ion, and it is on a general position. The NaF_6 coordination sphere, shown in Figure 4, is a very regular trigonal prism. The two triangular planes are parallel to within 0.4°. The Na–F distances range from 2.29(3) to 2.45(3) Å (the sum of bond valence contributions^{59–61} from these six F atoms is 0.92; the next shortest Na…F distance is 3.09(3) Å). Six Na⁺ ions surround the B1/B2 anions, and nine Na⁺ ions surround the B3–B6 anions. The anions in Na₂B₁₂F₁₂ are arranged in close-packed layers in which the B₁₂ centroids $(\odot s)$ are rigorously coplanar. The hexagonal arrays of $\odot s$ are offset from one another but do not form either cubic closepacked (CCP) or hexagonal close-packed (HCP) lattices, as shown in Figure 2. In fact, this type of offset produces an idealized body-centered cubic array of anions, as shown in Figure 6. The cubes are quite regular: the angles at cube corners only vary from 89.3 to 91.8°, and the two types of cube edge \odot ... \odot distances are 8.361 and 8.549 Å.

The compound $Na_2(B_{12}F_{12})$ is only the second anhydrous metal-ion salt of $B_{12}F_{12}^{2-}$ to be structurally characterized. Its



Figure 3. Drawings showing the hexagonal arrays of B_{12} centroids (large spheres) and the arrangement of Na^+ ions and H_2O ligands in the structures of $Na_2(H_2O)_4(B_{12}H_{12})$, $Na_2(H_2O)_4(B_{12}F_{12})$, and $Na_2(H_2O)_6(B_{12}Cl_{12})$. The H atoms were omitted from the H_2O molecules for clarity. Both the upper and lower sets of three drawings are to scale.



Figure 4. Drawings of the coordination spheres in $Na_2(B_{12}X_{12})$ (X = D, F, Cl), $Na_2(H_2O)_4(B_{12}X_{12})$ (X = H, F), and $Na_2(H_2O)_6(B_{12}Cl_{12})$. The thermal ellipsoid plots for $Na_2(H_2O)_4(B_{12}F_{12})$ and $Na_2(H_2O)_6(B_{12}Cl_{12})$ are drawn with 50% probability ellipsoids for Na and O atoms (H atoms are shown as spheres of arbitrary size). The Na…Na distances in the three $Na_2(H_2O)_n(B_{12}X_{12})$ structures are all 3.57 ± 0.08 Å (see Table 2).



Figure 5. Plot showing the 15 unique experimental B–B distances in the SC-XRD structures of Na₂(H₂O)₆(B₁₂Cl₁₂) (this work) and K₂(H₂O)₄(B₁₂F₁₂) (ref 50). The error bars shown are $\pm 3\sigma$. The horizontal lines indicate the DFT-predicted distances for I_h -B₁₂X₁₂^{2–} clusters from refs 50 (X = F) and 57 (X = Cl). Thermal ellipsoid drawings of the B₁₂Cl₁₂^{2–} anion in Na₂(H₂O)₆(B₁₂Cl₁₂) and the B₁₂F₁₂^{2–} anion in K₂(H₂O)₄(B₁₂F₁₂) are also shown (50% probability ellipsoids).

pseudo-BCC anion packing motif is significantly different than the HCP anion packing in $K_2(B_{12}F_{12})$.¹⁸ The Ni₂In-type structure^{62,63} of $K_2(B_{12}F_{12})$ has half of the K⁺ in O_h interstices and half in D_{3h} interstices within the close-packed layers of anions.¹⁸ Both types of K⁺ ions have KF₈ coordination spheres, but the O_h -hole K⁺ ions have an unusually small bond-valence sum, 0.73 (the sum for the D_{3h} -hole K⁺ ions is 1.11).¹⁸

The structure of $Na_2(B_{12}F_{12})$ is also significantly different than the structures of $Na_2B_{12}D_{12}$ and $Na_2B_{12}Cl_{12}$, as shown in Figure 2. The former compound has an antifluorite structure consisting of a CCP lattice of $B_{12}D_{12}^{2-}$ anions with Na^+ ions off-center in all of the T_d holes.⁴⁷ The latter compound has a CCP lattice of $B_{12}Cl_{12}^{2-}$ anions. Pairs of Na^+ ions fill all of the O_h holes, 5.662 Å apart, as shown in Figure 7. The NaCl₆ coordination sphere is shown in Figure 4. None of the Cl atoms bridge two Na^+ ions. The structure of $Na_2(B_{12}Cl_{12})$ is almost identical to the published structure of $Ag_2(B_{12}Cl_{12})$,⁶⁴ as shown in Figure S2. Both compounds crystallize in the $Pa\overline{3}$ space group. For $Na_2(B_{12}Cl_{12})$: $\bigcirc \dots \bigcirc = 8.82$ Å; perpendicular distance between close-packed planes of $\bigcirc s = 7.20$ Å; closest $Na \dots \bigcirc = 5.15$ Å; closest $Na \dots Na = 5.66$ Å; Na - Cl = 2.86(1)(×3) and 2.896(6) (×3) Å. For $Ag_2(B_{12}Cl_{12})$: $\odot \dots \odot = 8.76$ Å; perpendicular distance between close-packed planes of $\odot s =$ 7.15 Å; closest $Ag \dots \odot = 5.11$ Å; closest $Ag \dots Ag = 5.62$ Å; Ag -



Figure 6. Packing of anions and cations in anhydrous $Na_2(B_{12}F_{12})$ (B and F atoms omitted for clarity). The large spheres represent B_{12} centroids (\odot) , which form pseudo-BCC arrays. The open and shaded large spheres are \odot s of the B3–B6 and B1/B2 $B_{12}F_{12}^{2-}$ anions, respectively. The small shaded spheres represent Na^+ ions, and the very small black dots are the centroids of each of the six faces of the cubes. The drawings at the bottom are views looking down the crystallographic *c* axis. The drawing on the left shows a pseudobody-centered cube with a central B3–B6 \odot on a crystallographic 3 position. Note the three B1/B2 \odot s that are located at the midpoints of three unit cell *c* edges. The drawing on the right shows a cube with a central B1/B2 \odot located at the midpoint of a unit cell *c* edge (i.e., a crystallographic $\overline{3}$ position).



Figure 7. Drawing of the rigorous CCP array of B_{12} centroids (\odot) and the packing of Na⁺ ions in the structure of Na₂(B_{12} Cl₁₂). The \odot ··· \odot distances are 8.817 Å, and the \odot ··· \odot ·· \odot angles are exactly 60°. The perpendicular distance between the close-packed layers of \odot s is 7.199 Å.

Cl = 2.825 (×3) and 2.851 (×3) Å.⁶⁴ Note that the Shannon– Prewitt six-coordinate radii of Na⁺ and Ag⁺ are 1.16 and 1.29 Å, respectively.^{65,66} Similarly, the structure of Li₂(B₁₂H₁₂) has the same *Pa*3 CCP array of anions with pairs of Li⁺ ions sharing all of the *O_h* holes.⁶⁷ For Li₂(B₁₂H₁₂): $\bigcirc \cdots \bigcirc = 6.77$ Å; perpendicular distance between close-packed planes of $\bigcirc s =$ 5.53 Å; closest Li… $\bigcirc = 3.94$ Å; closest Li…Li = 4.65 Å; Li–H = 2.077(7) (×3) and 2.216(7) (×3) Å.⁶⁷

The structures of $Na_2(H_2O)_4(B_{12}F_{12})$ and $Na_{2}(H_{2}O)_{6}(B_{12}Cl_{12})$, like the structure of $Na_{2}(H_{2}O)_{4}(B_{12}H_{12})$, contain $[(H_2O)_2Na(\mu-H_2O)_2Na(H_2O)_2]^{2+}$ moieties with each Na⁺ ion also coordinated to two F or Cl atoms or two or three H atoms, as shown in Figures 3 and 4. There are four unique (but structurally very similar) Na⁺ ions in Na₂(H₂O)₄(B₁₂F₁₂) and two unique (but structurally very similar) Na⁺ ions in $Na_2(H_2O)_6(B_{12}Cl_{12})$. (Two of the three unique Na⁺ ions in $Na_2(H_2O)_4(B_{12}H_{12})$ have two Na-H bonds, and the third unique Na⁺ ion has three Na-H bonds. The Na⁺ ions shown in Figure 4 are the third type.) In $Na_2(H_2O)_4(B_{12}F_{12})$ and $Na_{2}(H_{2}O)_{4}(B_{12}H_{12})$, the $[(H_{2}O)_{2}Na(\mu-H_{2}O)_{2}Na(H_{2}O)_{2}]^{2+}$ moieties are joined into $\{[Na(\mu-H_2O)_2Na(\mu-H_2O)_2)]^{2+}\}_{\infty}$ infinite chains that run parallel to the crystallographic c axis between idealized close-packed arrays of $B_{12}X_{12}^{2^{-}}$ arions (X = F, H). In Na₂(H₂O)₆(B₁₂Cl₁₂), the [(H₂O)₂Na(μ -H₂O)₂Na $(H_2O)_2$ ²⁺ moieties are discrete cations with OH···O hydrogen bonds linking the terminal H₂O ligands of neighboring moieties into infinite hydrogen-bonded chains that run parallel to the crystallographic b axis between idealized close-packed arrays of $B_{12}Cl_{12}^{2-}$ anions. The perpendicular distances between the close-packed planes of anion centroids are 8.05, 7.69, and 7.04 Å in $Na_2(H_2O)_6(B_{12}Cl_{12})$, $Na_2(H_2O)_4(B_{12}F_{12})$, and Na2(H2O)4(B12H12), respectively (cf. 7.20, 6.01, and 5.78 Å in anhydrous $Na_2(B_{12}Cl_{12})$, $Na_2(B_{12}F_{12})$, and $Na_2(B_{12}D_{12})$, respectively).

Relative Coordinating Strength of B₁₂F₁₂²⁻, B₁₂Cl₁₂²⁻, and $B_{12}H_{12}^{2-}$. The fact that all three hydrates have $Na(H_2O)_4^+$ cations coordinated to $B_{12}X_{12}^{2-}$ anions provides a unique opportunity to quantitatively compare the coordinating strength of these three weakly coordinating anions to the same metal ion in the solid state. The bond-valence sums for the Na-O and Na-X bonds are listed in Table 2. The individual bond valence values are listed in Tables S3, S5, and S7. The significant figures of merit are the percentages of the total bond valence $(\% \Sigma(bv))$ due to the four Na–O bonds, which are 89% for $Na_2(H_2O)_6(B_{12}Cl_{12})$ (average of 85 and 93%), 75% for $Na_2(H_2O)_4(B_{12}H_{12})$ (average of 74, 76, and 76%), and 71% for $Na_2(H_2O)_4(B_{12}F_{12})$ (average of four values that range from 70 to 73%). Therefore, the % \sum (bv) values due to the anions are 11%, 25%, and 29% for $B_{12}Cl_{12}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_{12}F_{12}^{2-}$ in these three compounds, respectively. By this criterion, the $B_{12}Cl_{12}^{2-}$ anion is significantly more weakly coordinated to Na⁺ in the solid state than either $B_{12}H_{12}^{2-}$ or $B_{12}F_{12}^{2-}$. Interestingly, Knapp and co-workers have shown that $B_{12}F_{12}^{2-}$ is significantly less basic toward the N–H bond in the N(octyl)₃H⁺ ion than is $B_{12}Cl_{12}^{2-.58}$

A related comparison is the % \sum (bv) values due to the anions in K₂(SO₂)₆(B₁₂F₁₂) (six K–OSO and two K–F bonds for each K⁺ ion)²¹ and K₂(SO₂)₈(B₁₂Cl₁₂) (six K–OSO and three K–Cl bonds for each K⁺ ion).⁵⁸ These values are 28 and 24% in the B₁₂F₁₂²⁻ and B₁₂Cl₁₂²⁻ compounds, respectively. In this case, on the one hand, the structures also indicate that B₁₂Cl₁₂²⁻ is more weakly coordinating than B₁₂F₁₂²⁻ (i.e., to K⁺ in the solid state), although the difference between the anions is much smaller than it is for Na⁺ coordinated to Ag⁺ in the solid state than B₁₂F₁₂²⁻, since crystallization of Ag₂(B₁₂Cl₁₂) and Ag₂(B₁₂F₁₂) from H₂O produces anhydrous Ag₂(B₁₂Cl₁₂)⁶⁴ but hydrated Ag₂(H₂O)₄(B₁₂F₁₂).²¹

Thermal Behavior of $Na_2(B_{12}F_{12})$, $Na_2(H_2O)_4(B_{12}F_{12})$, and $Na_2(H_2O)_6(B_{12}Cl_{12})$. Part of the heating and cooling DSC trace of a sample of $Na_2(B_{12}F_{12})$ is shown in Figure 8. The



Figure 8. Heating and cooling DSC traces for a ca. 5 mg sample of $Na_2(B_{12}F_{12})$. Only the relative heat-flow changes between 500 and 600 K (227 and 327 °C) are shown. The heating and cooling rate was 20 K min⁻¹. The endothermic feature at ca. 560 K (ca. 287 °C) during the heating phase of the experiment was reversible when cooled with no significant hysteresis.

endothermic feature upon heating with a peak temperature of ca. 560 K (ca. 287 °C) presumably marks the transition to a disordered phase. When cooled, the reversion back to the ordered $P\overline{3}$ structure occurs with no significant hysteresis. The occurrence of a structural transition is consistent with the known order-disorder transition observed for $Na_2(B_{12}H_{12})$ at 529 K⁴⁷ and for the presumed order-disorder transitions observed by DSC for $Na_2(B_{12}Cl_{12})$ and $Na_2(B_{12}I_{12})$ at 730 and 816 K, respectively.⁶⁸ The new result for $Na_2(B_{12}F_{12})$ demonstrates that the transition temperature decreases monotonically as the size and mass of the X substituents decrease from I to Cl to F to H. On the basis of the previously observed structural behavior and superionic conductivity of various Li⁺ and Na⁺ closo-hydroborane salts,^{42-45,47} the presumed disordered phases of $Na_2(B_{12}F_{12})$, $Na_2(B_{12}Cl_{12})$, and $Na_2(B_{12}I_{12})$ are also likely to be cubic (FCC or BCC) or hexagonal stacking arrangements of orientationally disordered and orientationally mobile anions with vacancy-rich cation sublattices, which may result in fast-ion conduction.

Thermogravimetric analysis (TGA) of samples of Na₂(H₂O)₄(B₁₂F₁₂) and Na₂(H₂O)₆(B₁₂Cl₁₂) are shown in Figures 9 and 10, respectively. The hydration reaction Na₂(B₁₂F₁₂)(s) + 4 H₂O(g) \rightarrow Na₂(H₂O)₄(B₁₂F₁₂)(s) was complete at 21(1) °C when the vapor pressure of H₂O (*P*(H₂O)) was 17(1) torr (saturated aqueous BaCl₂ at 21(1) °C). However, in dry N₂ at 25 °C only the first two H₂O ligands per formula unit were lost at an appreciable rate, suggesting the existence of the new hydration phase Na₂(H₂O)₂(B₁₂F₁₂), which may have a structure similar to that of K₂(H₂O)₂(B₁₂F₁₂).¹⁴ Heating the sample from 25 to 150 °C resulted in complete dehydration of Na₂(H₂O)₂(B₁₂F₁₂) to Na₂(B₁₂F₁₂) within minutes.

The loss of two of the four coordinated H₂O molecules at room temperature in only 30 min is significant. Very few salt hydrates or hydrated alkali-metal ions in mesoporous materials (e.g., MOFs, zeolites) undergo even partial dehydration in only minutes at 25 °C (see ref 14 and refs therein). A relevant example is the crystalline layered silicate $Na_8(H_2O)_{32}Si_{32}$ -O₆₄(OH)₈, with four molecules of H₂O of hydration per Na⁺ ion, half of which are shared with neighboring Na⁺ ions.⁶⁹

Unlike Na₂(H₂O)₄(B₁₂F₁₂), this compound did not lose *any* H₂O during 30 min in dry N₂ at 25 °C. Instead, two of the four coordinated H₂O molecules per Na⁺ were removed between 40 and 75 °C. The remaining H₂O molecules were removed by heating above 100 °C.⁶⁹



Figure 9. TGA plot for Na₂(H₂O)₄(B₁₂F₁₂). The sample was prepared by treating Na₂(B₁₂F₁₂) with 17(1) torr H₂O(g) at 21(1) °C for 4 h. It was removed from the 17 torr H₂O(g) chamber, weighed, and placed in the TGA furnace within minutes. The sample rapidly lost mass at a nearly constant rate at 25 °C in dry N₂ for ca. 30 min, at which time the stoichiometry was precisely Na₂(H₂O)₂(B₁₂F₁₂). Further mass loss was negligible at 25 °C. Heating the sample to 150 °C resulted in complete dehydration to Na₂(B₁₂F₁₂) in less than 20 min (note that significant mass loss occurred only after the temperature reached ca. 75 °C).



Figure 10. TGA plot for $Na_2(H_2O)_6(B_{12}Cl_{12})$. The sample was prepared by treating $Na_2(B_{12}Cl_{12})$ with 6(1) torr $H_2O(g)$ at 21(1) °C for 14 h. It was removed from the 6 torr $H_2O(g)$ chamber, weighed, and placed in the TGA furnace within minutes. The sample lost mass at a nearly constant rate at 25 °C in dry N_2 for ca. 2 h, at which time the stoichiometry was approximately $Na_2(H_2O)_2(B_{12}Cl_{12})$. Unlike $Na_2(H_2O)_2(B_{12}F_{12})$ (see Figure 9), $Na_2(H_2O)_2(B_{12}Cl_{12})$ continued to lose mass at 25 °C but at a significantly slower rate than the initial change in mass from $Na_2(H_2O)_6(B_{12}Cl_{12})$ to approximately $Na_2(H_2O)_2(B_{12}Cl_{12})$. Heating the sample to 75 °C resulted in complete dehydration to $Na_2(B_{12}Cl_{12})$ within 15 min.

The hydration reaction Na₂(B₁₂Cl₁₂)(s) + 6 H₂O(g) \rightarrow Na₂(H₂O)₆(B₁₂Cl₁₂)(s) was complete at 21(1) °C when the vapor pressure of H₂O (*P*(H₂O)) was 6(1) torr (saturated aqueous MgCl₂ at 21(1) °C; the compound Na₂(B₁₂Cl₁₂) is deliquescent in the presence of 17(1) torr H₂O(g)). The

hexahydrate also lost H₂O in dry N₂ at 25 °C but at a slower rate than Na₂(H₂O)₄(B₁₂F₁₂). It lost four of the six molecules of coordinated H₂O at a nearly constant rate during 120 min, and the putative intermediate dihydrate phase Na₂(H₂O)₂(B₁₂Cl₁₂) continued to lose H₂O at 25 °C but at a much slower rate. Heating the sample from 25 to 75 °C resulted in complete dehydration of Na₂(H₂O)₂(B₁₂Cl₁₂) to Na₂(B₁₂Cl₁₂) within minutes.

The packing of $B_{12}F_{12}^{2-}$ anions in both hydrated $Na_2(H_2O)_4(B_{12}F_{12})$ and anhydrous $Na_2(B_{12}F_{12})$ can be represented as pseudobody-centered-cubic (pseudo-BCC) arrays, as shown in Figure 11. In $Na_2(B_{12}F_{12})$, the "cubic"



Figure 11. Portions of the structures of Na₂(H₂O)₄(B₁₂F₁₂) (top) and Na₂(B₁₂F₁₂) (bottom), showing the structural changes that occur during dehydration (H atoms omitted for clarity). The green spheres are B₁₂ centroids (\odot), the blue spheres are Na⁺ ions, the red spheres are O atoms, and the small black dots are the centroids of the cube-like prism faces (only four of the six face centroids are depicted in the top drawing, and, for clarity, the Na⁺ ions, O atoms, and face centroids are only shown in one of the two adjacent pseudo-BCC prisms in each drawing).

arrays are surprisingly regular. The angles at the corners of the cube-like prisms only vary from 89.3 to 91.8°. The prism edge $\bigcirc \cdots \bigcirc$ distances are 8.361 and 8.549 Å. The pseudo-BCC prisms in Na₂(H₂O)₄(B₁₂F₁₂) are not nearly as regular. The angles at the prism corners vary from 83.5 to 96.5°, and the prism edge $\bigcirc \cdots \bigcirc$ distances are 10.850, 10.649, and 6.955 Å, which are equal to the unit cell *a*, *b*, and *c*/2 dimensions. The $\{[Na(\mu-H_2O)_2Na(\mu-H_2O)_2)]^{2+}\}_{\infty}$ infinite chains are parallel to the crystallographic *c* axis and are centered on four of the six faces of the pseudo-BCC prisms (note that the small solid black dots in Figure 11 are the centroids of the prism faces, which in Na₂(H₂O)₄(B₁₂F₁₂) are also the centroids of the Na₂(H₂O)₆²⁺ moieties shown in the figure).

Figure 11 shows that only a relatively small lattice rearrangement occurs when $Na_2(H_2O)_4(B_{12}F_{12})$ undergoes complete dehydration to $Na_2(B_{12}F_{12})$. The anions remain in a pseudo-BCC array as the lattice contracts by ca. 23% when the H₂O molecules leave (the effective volume of each H₂O molecule is 22.2 Å³ (i.e., $(1/4)[(1/4)(1577.0 Å^3) - (1/3)(916.5 Å^3)] = 22.2 Å^3)$). The pairs of Na⁺ ions in the $Na_2(H_2O)_2^{2^+}$ moieties, which are 3.56–3.61 Å apart, must

separate and move into empty spaces between the anions, where the shortest Na…Na distances are 5.28 Å.

Portions of the structures of $Na_2(H_2O)_6(B_{12}Cl_{12})$ and $Na_2(B_{12}Cl_{12})$ that depict the structural changes that occur during dehydration are shown in Figure 12. The pseudo-BCC



Figure 12. Portions of the structures of Na₂(H₂O)₆(B₁₂Cl₁₂) (top) and Na₂(B₁₂Cl₁₂) (bottom), showing the structural changes that occur during dehydration (H atoms omitted for clarity). The green spheres are B₁₂ centroids (\odot), the blue spheres are Na⁺ ions, the red spheres are O atoms, and the small black spheres are the centroids of the cube-like prism faces in the top drawing. The Na⁺ ions, O atoms, and face centroids are only shown in one of the two adjacent BCC prisms in the top drawing for clarity. The bottom drawing shows two adjacent face-centered cubes of anion \odot s, both of which are shown with pairs of Na⁺ ions that are 5.66 Å apart. The solid line connecting the pairs of Na⁺ ions is a visual aid and has no other significance.

array of anions in Na₂(H₂O)₆(B₁₂Cl₁₂) must rearrange into the rigorous FCC anion array in Na₂(B₁₂Cl₁₂) as the lattice contracts by ca. 25% when the H₂O molecules leave (the effective volume of each H₂O molecule is 25.0 Å³ (i.e., (1/6)[1/4(2580.0 Å³) - (1/4)(1980.3 Å³)] = 25.0 Å³)). The BCC-like prism $\bigcirc \cdots \odot$ distances in Na₂(H₂O)₆(B₁₂Cl₁₂) are 12.59, 11.55, and 8.92 Å (the short distance is the crystallographic *b* axis, which is parallel to the Na…Na vectors), and the angles at the prism corners are 83.9, 90.0, and 96.1°. The drawing of Na₂(B₁₂Cl₁₂) in Figure 12 shows two adjacent face-centered cubes of anion \bigcirc s, both of which are shown with pairs of Na⁺ ions that are 5.66 Å apart. The cube $\bigcirc \cdots \odot$ distances are 12.47 Å.

Compared to the small lattice rearrangement upon dehydration of Na₂(H₂O)₄(B₁₂F₁₂) to Na₂(B₁₂F₁₂), the dramatic change in anion array packing upon dehydration of Na₂(H₂O)₆(B₁₂Cl₁₂) to Na₂(B₁₂Cl₁₂) is consistent with the weaker coordinating strength of B₁₂Cl₁₂²⁻ relative to B₁₂F₁₂²⁻. To enhance the interactions between B₁₂Cl₁₂²⁻ and Na⁺ so as to maintain a crystal structure after dehydration from Na₂(H₂O)₆(B₁₂Cl₁₂) to Na₂(B₁₂Cl₁₂), the Na–Cl bond distances are reduced from 3.093 and 3.311 Å in the pseudo-BCC anion array in Na₂(H₂O)₆(B₁₂Cl₁₂) (see Tables S4 and S5). In constrast, the average Na–F bond distances in Na₂(H₂O)₄(B₁₂F₁₂) and Na₂(B₁₂Cl₁₂) are essentially the same, 2.37 and 2.38 Å, respectively (see Tables S2 and S3). An additional manifestation of the weaker coordinating strength of

 $B_{12}Cl_{12}{}^{2-}$ is that the anhydrous salt $Na_2(B_{12}Cl_{12})$ is fully hydrated to $Na_2(H_2O)_6(B_{12}Cl_{12})$ in the presence of 6(1) torr $H_2O(g)$, but $Na_2(B_{12}F_{12})$ is only partially hydrated to $Na_2(H_2O)_2(B_{12}F_{12})$ under 6(1) torr $H_2O(g)$.

CONCLUSIONS

The structures and thermal behavior of $Na_2(H_2O)_4(B_{12}F_{12})$, $Na_2(B_{12}F_{12})$, $Na_2(H_2O)_6(B_{12}Cl_{12})$, and $Na_2(B_{12}Cl_{12})$ demonstrate in three different ways that the $B_{12}Cl_{12}^{2-}$ anion is more weakly coordinating to Na⁺ in the solid state than its fluorinated congener $B_{12}F_{12}^{2-}$. (1) The contributions to the sums of Na⁺ bond valences due to the Na-X bonds in the $NaX_{2}(H_{2}O)_{4}$ complexes are 11 and 29% in $Na_2(H_2O)_6(B_{12}Cl_{12})$ and $Na_2(H_2O)_4(B_{12}F_{12})$, respectively. (2) The Na-Cl bonds in the NaCl₆ coordination sphere in $Na_2(B_{12}Cl_{12})$ are significantly shorter than the Na–Cl bonds in the NaCl₂(H₂O)₄ coordination sphere in Na₂(H₂O)₆(B₁₂Cl₁₂), whereas the Na-F bonds in the NaF₆ coordination spheres in $Na_2(B_{12}F_{12})$ and the $NaF_2(H_2O)_4$ coordination spheres in $Na_2(H_2O)_4(B_{12}F_{12})$ are essentially the same length. (3) Anhydrous $Na_2(B_{12}Cl_{12})$ undergoes complete hydration to $Na_2(H_2O)_6(B_{12}Cl_{12})$ under 6 torr of $H_2O(g)$ and is deliquescent under 17 torr of $H_2O(g)$, whereas $Na_2(B_{12}F_{12})$ only undergoes partial hydration to $Na_2(H_2O)_2(B_{12}F_{12})$ under 6 torr of $H_2O(g)$ and requires 17 torr of $H_2O(g)$ to become fully hydrated $Na_2(H_2O)_4(B_{12}F_{12})$. The weaker coordination of $B_{12}Cl_{12}^{2-}$ to hard Na⁺ than $B_{12}F_{12}^{2-}$ is the counterpoint to the stronger coordination of $B_{12}Cl_{12}^{2-}$ to soft Ag⁺ than $B_{12}F_{12}^{2-}$ (vide supra).

In addition, the structural and thermal behavior studies reported in this paper show that these compounds have properties that may find use in applications, such as hydration/ dehydration thermal energy storage $(Na_2(H_2O)_4(B_{12}F_{12}))$ and $Na_2(H_2O)_6(B_{12}Cl_{12})$, as models for kinetic studies if not for actual deployment in practical devices) and as components or starting materials for solid-state electrolytes for Na⁺ ion batteries $(Na_2(B_{12}F_{12}))$ and $Na_2(B_{12}Cl_{12}))$. As far as the latter application is concerned, their greater than or equal to 560 K transition temperatures preclude their use as pure, coarsely crystalline materials. Nevertheless, in previous work we have shown that superionic disordered phases can be stabilized at or below room temperature by (i) forming mixtures of different high-transition-temperature salts⁴⁶ or (ii) nanosizing and disordering the pure, coarsely crystalline compounds by ballmilling.⁷⁰ Thus, the various halogenated *closo*-borane cluster compounds, including $Na_2(B_{12}F_{12})$ and $Na_2(B_{12}Cl_{12})$, with their relatively high stabilities, overly large anion sizes, and weak interactions with the surrounding cations, may still be potentially effective building blocks in the synthesis of future hybrid, solid superionic materials for energy-storage applications. Such experiments with halogenated $Na_2(B_{12}X_{12})$ salts are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02920.

NPD pattern, structure comparison, bond valence parameters, bond distances, bond valences, crystal data and refinement parameters, NMR spectra (PDF) X-ray crystallographic information (CIF) X-ray crystallographic information (CIF) X-ray crystallographic information (CIF) X-ray crystallographic information (CIF) X-ray crystallographic information (CIF)

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

Comparison of the Coordination of $B_{12}F_{12}^{2-}$, $B_{12}Cl_{12}^{2-}$, and $B_{12}H_{12}^{2-}$ to Na⁺ in the Solid State: Crystal Structures and Thermal Behavior of Na₂(B₁₂F₁₂), Na₂(H₂O)₄(B₁₂F₁₂), Na₂(B₁₂Cl₁₂), and Na₂(H₂O)₆(B₁₂Cl₁₂)

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W. Matthew Jones, Vitalie Stavila, Terrence J. Udovic, and Steven H. Strauss

Table of Contents

	page
Figure S1. 295 K NPD pattern for Na ₂ (B ₁₂ Cl ₁₂)	S2
Figure S2. Comparison of the structures of Na ₂ (B ₁₂ Cl ₁₂) and Ag ₂ (B ₁₂ Cl ₁₂)	S 3
Table S1. Bond valence parameters used in this work	S 4
Table S2. Bond distances and bond valences for $Na_2(B_{12}F_{12})$	S4
Table S3. Bond distances and bond valences for $Na_2(H_2O)_4(B_{12}F_{12})$	S4
Table S4. Bond distances and bond valences for Na ₂ (B ₁₂ Cl ₁₂)	S5
Table S5. Bond distances and bond valences for Na ₂ (H ₂ O) ₆ (B ₁₂ Cl ₁₂)	S5
Table S6. Bond distances and bond valences for Na ₂ (B ₁₂ D ₁₂)	S5
Table S7. Bond distances and bond valences for $Na_2(H_2O)_4(B_{12}H_{12})$	S6
Table S8. Crystal Data and Final Refinement Parameters for Single-Crystal X-ray	
and Neutron Powder Diffraction Structures, including the literature structures	
$Na_2(B_{12}D_{12})$ and $Na_2(H_2O)_4(B_{12}H_{12})$	S 7
Figure S3. NMR spectra of anhydrous $Na_2(B_{12}F_{12})$ (heated at 175 °C for 24 h)	S 8
Figure S4. Proton NMR spectra of anhydrous Na ₂ (B ₁₂ Cl ₁₂) (heated at 150 °C for 18 h)	S 9
Figure S5. Boron-11 NMR spectra of anhydrous $Na_2(B_{12}Cl_{12})$ before and after heating	S10



Figure S1. Experimental (circles), fitted (red trace), and difference (black trace) neutron powder diffraction (NPD) patterns for $Na_2(B_{12}Cl_{12})$ at 295 K. Vertical bars at are the calculated positions of NPD Bragg peaks for $Na_2(B_{12}Cl_{12})$ (upper set of bars) and for the vanadium sample holder (lower set of bars). See Table 1 in the main text for additional information.



Figure S2. Comparison of the nearly identical $Pa\overline{3}$ structures of Na₂(B₁₂Cl₁₂) (this work; 5 K NPD) and Ag₂(B₁₂Cl₁₂) (Tiritiris and Schleid; ref 60 in the main text; 295 K SC-XRD). For clarity only the B₁₂ centroids (\odot) and two metal ions are shown in the upper drawings. The lower drawings are two perpendicular views of the NaCl₆ and AgCl₆ coordination spheres. In these structures pairs of metal ions share the octahedral interstices formed by the rigorous CCP array of B₁₂Cl_{12²⁻} anions. For Na₂(B₁₂Cl₁₂): $\odot \cdots \odot = 8.82$ Å; perpendicular distance between close-packed planes of \odot 's = 7.20 Å; closest Na $\cdots \odot = 5.15$ Å; closest Na $\cdots Na = 5.66$ Å; Na–Cl = 2.86(1) (×3) and 2.896(6) (×3) Å. For Ag₂(B₁₂Cl₁₂): $\odot \cdots \odot = 8.76$ Å; perpendicular distance between close-packed planes of \odot 's = 7.15 Å; closest Ag $\cdots \odot = 5.11$ Å; closest Ag \cdots Ag = 5.62 Å; Ag–Cl = 2.825 (×3) and 2.851 (×3) Å.

cation	R _{NaF}	<i>R</i> _{NaO}	R _{NaCl}	R _{NaH(D)}	
Na^+	1.80	1.805	1.85	1.85	

Table S1. Bond valence parameters used in this work for Na–X distances $(X = F, O, N, C, Cl)^a$

^a The bond valence contribution for each Na–X distance (i.e., bv(NaX); X = F, O, Cl, and H(D)) is calculated using the formula $bv(NaX) = exp[(R_{NaX} - d_{NaX})/0.37]$, where d_{NaX} is the Na–X distance. The R_{NaX} values were taken from Brese, N. E.; O'Keeffe, M. *Acta Cryst.* **1991**, *B47*, 192–197.

Table S2. Na–F bond distances and bond valences for Na₂(B₁₂F₁₂) (this work)

Na2(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)
this work (NPD)	Na-F7	2.45	1.677	0.124	0.134
	Na-F8	2.42	1.677	0.134	0.146
	Na-F9	2.44	1.677	0.127	0.138
	Na-F10	2.29	1.677	0.191	0.207
	Na-F11	2.41	1.677	0.138	0.150
	Na-F12	2.26	1.677	0.207	0.225
			Σ(bv) =	0.921	

Table S3. Na–O and Na–F bond distances and bond valences for $Na_2(H_2O)_4(B_{12}F_{12})$ (this work)

Na2(H2O)4(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)	bond	distance	bv param	bv	bv/Σ(bv)
this work (SC-XRD)	Na1-01	2.367	1.803	0.218	0.192	Na2-05	2.369	1.803	0.217	0.203
	Na1-O2	2.401	1.803	0.199	0.175	Na2-07	2.451	1.803	0.174	0.163
	Na1-06	2.413	1.803	0.192	0.169	Na2-01	2.473	1.803	0.164	0.154
	Na1-08	2.427	1.803	0.185	0.163	Na2-08	2.412	1.803	0.193	0.181
	Na1-F11	2.348	1.677	0.163	0.144	Na2-F10	2.343	1.677	0.165	0.155
	Na1-F12	2.314	1.677	0.179	0.157	Na2-F22	2.372	1.677	0.153	0.144
			Σ(bv) =	1.136				Σ(bv) =	1.065	
			Σ(Na-O bv) =	0.794	0.699			Σ(Na-O bv) =	0.746	0.701
	bond	distance	bv param	bv	bv/Σ(bv)	bond	distance	bv param	bv	bv/Σ(bv)
	Na3-02	2.456	1.803	0.171	0.160	Na4-03	2.458	1.803	0.170	0.169
	Na3-03	2.395	1.803	0.202	0.188	Na4-04	2.404	1.803	0.197	0.195
	Na3-04	2.430	1.803	0.184	0.171	Na4-05	2.460	1.803	0.169	0.168
	Na3-06	2.373	1.803	0.214	0.200	Na4-07	2.405	1.803	0.197	0.195
	Na3-F19	2.380	1.677	0.150	0.139	Na4-F21	2.394	1.677	0.144	0.143
	Na3-F9	2.374	1.677	0.152	0.142	Na4-F23	2.423	1.677	0.133	0.132
			Σ(bv) =	1.073				Σ(bv) =	1.010	
				_						
			Σ(Na-O bv) =	0.771	0.719			Σ(Na-O bv) =	0.733	0.726

Na2(B12Cl12)	bond	distance	bv param	bv	bv/Σ(bv)
this work (NPD)	Na-Cl1	2.861	2.15	0.146	0.159
	Na-Cl1	2.861	2.15	0.146	0.159
	Na-Cl1	2.861	2.15	0.146	0.159
	Na-Cl2	2.896	2.15	0.133	0.145
	Na-Cl2	2.896	2.15	0.133	0.145
	Na-Cl2	2.896	2.15	0.133	0.145
			Σ(bv) =	0.839	

Table S4. Na–Cl bond distances and bond valences for Na₂(B₁₂Cl₁₂) (this work)

Table S5. Na–O and Na–Cl bond distances and bond valences for Na₂(H₂O)₆(B₁₂Cl₁₂) (this work)

Na2(H2O)6(B12Cl12)	bond	distance	bv param	bv	bv/Σ(bv)	bond	distance	bv param	bv	bv/Σ(bv)
this work (SC-XRD)) Na1-O1 2.316		1.803	0.250	0.235	Na2-O3	2.220	1.803	0.324	0.305
	Na1-01'	2.316	1.803	0.250	0.235	Na2-O3'	2.220	1.803	0.324	0.305
	Na1-O2	2.393	1.803	0.203	0.191	Na2-O2	2.359	1.803	0.223	0.210
	Na1-02'	2.393	1.803	0.203	0.191	Na2-O2'	2.359	1.803	0.223	0.210
	Na1-Cl1	3.093	2.150	0.078	0.074	Na2-Cl5	3.311	2.150	0.043	0.041
	Na1-Cl1'	3.093	2.150	0.078	0.074	Na2-Cl5'	3.311	2.150	0.043	0.041
			Σ(bv) =	1.062				Σ(bv) =	1.180	
										0.000
			2(Na-O bv) =	0.906	0.853			2(Na-O bv) =	1.093	0.926

Table S6. Na–D bond distances and bond valences for $Na_2(B_{12}D_{12})^a$

Na2(B12D12) (NPD)	bond	distance	bv param	bv	bv/Σ(bv)
Verdal et al. J. Solid State Chem. 2014	Na-D	2.320	1.68	0.177	0.187
	Na-D	2.302	1.68	0.186	0.197
	Na-D	2.251	1.68	0.214	0.226
	Na-D	2.884	1.68	0.039	0.041
	Na-D	2.445	1.68	0.126	0.134
	Na-D	2.468	1.68	0.119	0.126
	Na-D	2.600	1.68	0.083	0.088
	Na-D	2.525	1.68	0.102	0.108
			Σ(bv) =	1.046	

 $^{\rm a}$ Verdal et al. (see ref 43 in the main text). The isotopic composition of the anion was 99.5% $^{11}{\rm B}$ and 87% D.

Table S7. Na–O and Na–H bond distances and bond valences for $Na_2(H_2O)_4(B_{12}H_{12})^a$

Na2(H2O)4(B12H12)	bond	distance	bv param	bv	bv/Σ(bv)	bond	distance	bv param	bv	bv/Σ(bv)	bond	distance	bv param	bv	bv/Σ(bv)
Scholkopf dissertation	Na1-O	2.369	1.803	0.217	0.197	Na2-O	2.388	1.803	0.206	0.188	Na3-O	2.383	1.803	0.209	0.190
(Stuttgart 2011)	Na1-O	2.369	1.803	0.217	0.197	Na2-O	2.388	1.803	0.206	0.188	Na3-O	2.409	1.803	0.194	0.177
	Na1-O	2.399	1.803	0.200	0.181	Na2-O	2.395	1.803	0.202	0.184	Na3-O	2.367	1.803	0.218	0.199
	Na1-O	2.399	1.803	0.200	0.181	Na2-O	2.395	1.803	0.202	0.184	Na3-O	2.412	1.803	0.193	0.176
	Na1-H	2.423	1.68	0.134	0.122	Na2-H	2.405	1.68	0.141	0.128	Na3-H	2.478	1.68	0.116	0.105
	Na1-H	2.423	1.68	0.134	0.122	Na2-H	2.405	1.68	0.141	0.128	Na3-H	2.503	1.68	0.108	0.099
											Na3-H	2.936	1.68	0.034	0.031
			Σ(bv) =	1.101				Σ(bv) =	1.097				Σ(bv) =	1.071	
			Σ(NaO bv) =	0.833	0.757			Σ(NaO bv) =	0.815	0.743			Σ(NaO bv) =	0.814	0.760

^a T. Scholköpf, Ph.D. Dissertation, Univ. of Stuttgart (see ref 44 in the main text).

compound abbreviation	$Na_2(B_{12}F_{12})$	$Na_2(H_2O)_4(B_{12}F_{12})$	$Na_2(B_{12}Cl_{12})$	$Na_2(B_{12}Cl_{12})$	$Na_2(H_2O)_6(B_{12}Cl_{12})$	Na ₂ (B ₁₂ D ₁₂) ^b	$Na_2(H_2O)_4(B_{12}H_{12})^{c}$
formula	$B_{12}F_{12}Na_2$	$B_{12}F_{12}H_8Na_2O_4$	$B_{12}Cl_{12}Na_2 \\$	$B_{12}Cl_{12}Na_2$	$B_{12}Cl_{12}H_{12}Na_2O_6$	$B_{12}D_{12}Na_2$	$B_{12}H_{20}Na_2O_4$
formula wt., g mol ⁻¹	403.68	475.76	601.14	601.14	709.20	187.79	475.75
SC-XRD or NPD	NPD	SC-XRD	NPD	NPD	SC-XRD	NPD	SC-XRD
diffraction wavelength, Å	1.5397	0.71073	1.5398	1.5397	0.71073	1.54059	0.71073
<i>Т</i> , К	5(2)	120(2)	5(2)	295(2)	100(2)	7(2)	100
crystal system	hexagonal	triclinic	cubic	cubic	monoclinic	monoclinic	tetragonal
space group, Z	<i>P</i> 3, 3	$P\overline{1}, 4$	$Pa\overline{3}, 4$	$Pa\overline{3}, 4$	<i>C</i> 2/ <i>c</i> , 4	$P2_1/n, 2$	$P4_{2}2_{1}2, 4$
<i>a</i> , Å	12.0118(13)	10.6491(10)	12.4694(4)	12.5577(9)	16.1546(14)	6.9750(4)	9.9637(4)
<i>b</i> , Å	12.0118(13)	10.8501(10)	12.4694(4)	12.5577(9)	8.9220(8)	10.5367(6)	9.9637(4)
<i>c</i> , Å	7.3347(15)	13.8432(11)	12.4694(4)	12.5577(9)	17.9687(16)	6.9557(4)	26.825(1)
α, deg	90	96.813(3)	90	90	90	90	90
β, deg	90	96.479(3)	90	90	94.999(4)	95.959(4)	90
γ, deg	120	91.347(4)	90	90	90	90	90
V, Å ³	916.5(1)	1577.0(2)	1938.8(2)	1980.3(4)	2580.0(4)	508.44(5)	2663.1(2)
$ ho_{ m calc}, { m g cm}^{-3}$	2.194	2.004	2.059	2.016	1.826	1.311	1.296
$R(F) \ (I > 2\sigma(I))^{\rm d}$	0.0317	0.0666	0.0191	0.0156	0.0225	0.030	0.059
$wR(F^2)$ [all data] ^d	0.0388	0.2163	0.0236	0.0186	0.0515	0.036	0.140
GOF	1.10	1.046	1.04	0.93	1.071	not reported	1.113

Table 1. Crystal Data and Final Refinement Parameters for Single-Crystal X-ray and Neutron Powder Diffraction Structures^a

^a All results from this work unless otherwise indicated. This table is a duplicate of Table 1 but also includes two literature compounds. ^b From Verdal, N.; Her, J.-H.; Stavila, V.; Soloninin, A. V.; Babanova, O. A.; Skripov, A. V.; Udovic, T. J.; Rush, J. J. Complex high-temperature phase transitions in Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂. *J. Solid State Chem.* **2014**, *212*, 81-91. ^c Schölkopf, T., Synthese und Strukturaufklärung von Dodekahydro-*closo*-Dodekaboraten und hydroxylierten Derivaten, Ph.D. Dissertation, Universität Stuttgart, 2011.



Figure S-3. NMR spectra of a sample of $Na_2(B_{12}F_{12})$ heated under vacuum at 175 °C for 24 h. The compound 1,4-C₆H₄(CF₃)₂ was used as a H/F intensity internal standard. The ¹H NMR spectrum demonstrates that the sample of anhydrous $Na_2(B_{12}F_{12})$ contained a negligible amount of H₂O, which may have been due to unavoidable contamination by the ppm amount of H₂O vapor present in the glovebox atmosphere. The other spectra demonstrate that no decomposition of the $B_{12}F_{12}^{2-}$ anion had occured when the sample was heated (note that no undissolved solids were present when the solution was prepared).



Figure S-4. Proton NMR spectra of anhydrous CD₃CN and a solution of CD₃CN and Na₂(B₁₂Cl₁₂) that had been heated under vacuum at 150 °C for 18 h (the bottom pair of spectra are greatly expanded along the *y* axis). The ¹H spectrum of heated Na₂(B₁₂Cl₁₂) demonstrates that the sample contained a negligible amount of H₂O, which may have been due to unavoidable contamination by the ppm amount of H₂O vapor present in the glovebox atmosphere. The small peak marked with an asterisk is due to an unidentified impurity.



Figure S-5. Boron-11 NMR spectra in CD₃CN of anhydrous Na₂(B₁₂Cl₁₂) before (stored in a desiccator at 22 °C) and after heating at 150 °C under vacuum for 18 h. The spectra demonstrate that the $B_{12}Cl_{12}^{2-}$ anion was intact, and that no other boron-containing species were present, after heating (note that no undissolved solids were present when the solution was prepared).